

Supporting Information for  
Microscale Characterization of Sulfur Speciation in Lake  
Sediments

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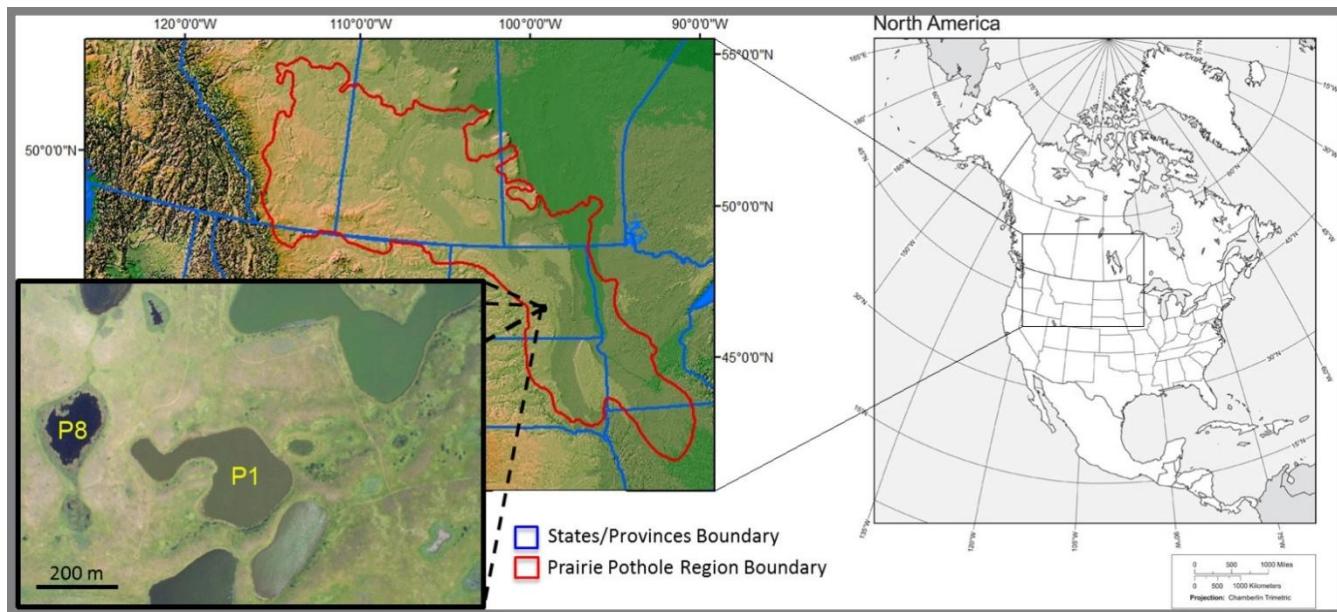
(Total 32 pages, 2 text, 10 tables, 4 figures)

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## 1. Field sampling and sample preparation (Figure S1)

The Cottonwood Lake study area (CLSA), which is situated on the eastern edge of a large glacial drift complex known as the *Missouri Coteau*, consists of a complex of sixteen temporary, seasonal, and semipermanent wetlands within a 91.8 ha hummocky prairie grassland.<sup>1-3</sup> The semi-arid climate of the CLSA is characterized by long, cold, dry winters and short, mild, wet summers, with a mean annual temperature of 4 °C and a mean annual precipitation of 440 mm.<sup>4</sup> Two semipermanent wetlands, P1 and P8 (Figure S1),<sup>1</sup> were chosen for this study because they are representative of the biological, chemical, and hydrological conditions in the CLSA.<sup>5</sup> Both P1 and P8 receive water from direct precipitation, groundwater recharge as well as runoff from surrounding uplands, while the greatest loss of water is through evapotranspiration.<sup>4,6</sup> P1 differs hydrologically from P8 in that it has a more dynamic water regime and a lower annual turnover of water due to the lack of an intermittent surface outlet.<sup>7</sup> As a result of the unique morphometry (area = 3.0–4.6 ha, mean depth < 2 m) and continuous wind-induced turbulence, the surface water of P1 and P8 remains aerobic throughout the year,<sup>8</sup> but the bottom water and sediment develop anoxic conditions.<sup>9</sup>



**Figure S1.** Location and photograph of Lakes P1 and P8 within the Cottonwood Lake study area (CLSA), North Dakota, USA. North America map courtesy of Douglas Minnis, Arizona Geographic Alliance and Arizona State University. Inset PPR and CLSA images courtesy of Dr. David N. Mushet, USGS Northern Prairie Wildlife Research Center.<sup>10</sup>

Replicate sediment cores were collected from benchmark locations (either from a mid-lake weather station in P1 or from an anchored boat in P8 to minimize the *horizontal* spatial variability) using a push corer and transported in sealed polycarbonate core liners to the University of Minnesota within 24 h for processing.<sup>11</sup> Immediately upon return to the laboratory, sediment cores were pressurized in a Jahnke-type core squeezer and profile porewaters at selected depths were extracted directly into argon-filled glass syringes.<sup>12</sup> Sediment cores were also sliced into Nalgene centrifuge bottles under a stream of nitrogen and centrifuged in a Beckman JA-10 rotor (3 times at 5000 rpm for 30 min) for bulk porewater collection.<sup>11</sup> Porewater samples were then immediately transferred into a glove box (95% N<sub>2</sub>/5% H<sub>2</sub>, Pd catalyst, Coy Laboratory Products Inc.) and sealed in acid-washed serum vials with minimal headspace. Consolidated sediment samples from the 5-30 cm depth interval were homogenized in the glove box (to minimize the *vertical* spatial variability), sealed in acid-washed glass jars, and kept frozen for solid phase chemical analyses.

Sediment samples for S XANES spectroscopy were prepared in the glove box under strictly anoxic conditions. Sediment samples were first dried to a constant weight in desiccators and ground and homogenized using an Agate mortar and pestle. The mortar and pestle were thoroughly rinsed with acetone and ultrapure water between samples to avoid cross contamination. For all samples, considerable care was taken to avoid artificial changes of redox-active species by oxidation during XANES analyses. Briefly, a thin layer of sediment was spread onto a 4.0 µm thick low-sulfur XRF film (Premier Lab Supply, Inc.) and sealed between two 3.6 µm thick low-sulfur Mylar X-ray films (Premier Lab Supply, Inc.). No visible formation of red/orange ferric (hydr)oxides was apparent for a ferrous sulfate solution (1 mM) sealed between Mylar X-ray films after a 24 h period of exposure to air, suggesting that such preservation approach was sufficient to maintain the redox integrity of samples. Sample film stacks were mounted on aluminum sample holders, which were subsequently sealed in 0.15 mm thick Mylar bags along with AnaeroPack oxygen scrubbers (Mitsubishi Gas Chemical Company, Inc.). The Mylar packages were transported within nitrogen-filled Mylar bags and stored under argon until XANES analyses. Subsamples of consolidated sediments were also sent to the Soil Testing Laboratory at the University of Minnesota for analyses of total S, organic matter, total organic carbon, and trace elements.

## 2. Sulfur functionality and XANES spectra of S reference compounds (Table S1 and Figure S2-S3)

**Table S1. Sulfur functionality, oxidation state, and white-line peak**

S functionality	S oxidation state	White-line peak (eV)	References
Iron monosulfide  S <sup>2-</sup>	-2	2468.9	Sugiura (1981) <sup>13</sup>
		2471.0	Vairavamurthy <i>et al.</i> (1995) <sup>14</sup>
		2470.2	Morra <i>et al.</i> (1997) <sup>15</sup>
		2470.8	Bostick <i>et al.</i> (2005) <sup>16</sup>
		2469.4	Burton <i>et al.</i> (2009) <sup>17</sup>
		2469.4	Prietzl <i>et al.</i> (2009) <sup>18</sup>
		2470.1	Orthous-Daunay <i>et al.</i> (2010) <sup>19</sup>
		2470.7	Prietzl <i>et al.</i> (2011) <sup>20</sup>
		2471.1	Hoffmann <i>et al.</i> (2012) <sup>21</sup>
		<b>2470.2 (±0.8)</b>	<b>Mean (±SD)</b>
Iron disulfide  S <sub>2</sub> <sup>2-</sup>	-1	2470.8	Sugiura (1981) <sup>13</sup>
		2472.2	Vairavamurthy <i>et al.</i> (1994) <sup>22</sup>
		2472.2	Vairavamurthy <i>et al.</i> (1995) <sup>14</sup>
		2472.5	Vairavamurthy <i>et al.</i> (1997) <sup>23</sup>
		2472.0	Sarret <i>et al.</i> (1999) <sup>24</sup>
		2471.8	Bostick <i>et al.</i> (2005) <sup>16</sup>
		2471.9	Prietzl <i>et al.</i> (2007) <sup>25</sup>
		2471.9	Lemelle <i>et al.</i> (2008) <sup>26</sup>
		2472.0	Burton <i>et al.</i> (2009) <sup>17</sup>
		2471.8	Orthous-Daunay <i>et al.</i> (2010) <sup>19</sup>
		2471.1	Prietzl <i>et al.</i> (2011) <sup>20</sup>
		2472.1	Hoffmann <i>et al.</i> (2012) <sup>21</sup>
		2472.2	Manceau and Nagy (2012) <sup>27</sup>
		<b>2471.9 (±0.5)</b>	<b>Mean (±SD)</b>

**Table S1. Sulfur functionality, oxidation state, and white-line peak (continued)**

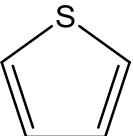
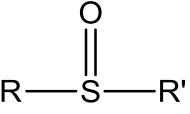
S functionality	S oxidation state	White-line peak (eV)	References
Elemental sulfur  $S^0$	0	2472.7	Waldo <i>et al.</i> (1991) <sup>28</sup>
		2472.6	Vairavamurthy <i>et al.</i> (1994) <sup>22</sup>
		2472.6	Vairavamurthy <i>et al.</i> (1995) <sup>14</sup>
		2472.5	Morra <i>et al.</i> (1997) <sup>15</sup>
		2472.5	Vairavamurthy <i>et al.</i> (1997) <sup>23</sup>
		2472.3	Bostick <i>et al.</i> (2005) <sup>16</sup>
		2472.4	Burton <i>et al.</i> (2009) <sup>17</sup>
		2471.7	Cai <i>et al.</i> (2009) <sup>29</sup>
		2472.7	Prietzl <i>et al.</i> (2009) <sup>18</sup>
		2472.7	Almkvist <i>et al.</i> (2010) <sup>30</sup>
		2472.5	Orthous-Daunay <i>et al.</i> (2010) <sup>19</sup>
		2472.6	Prietzl <i>et al.</i> (2011) <sup>20</sup>
		2472.8	Hoffmann <i>et al.</i> (2012) <sup>21</sup>
		2472.6	Manceau and Nagy (2012) <sup>27</sup>
<b>2472.5 (<math>\pm 0.3</math>)</b>		<b>Mean (<math>\pm SD</math>)</b>	
Organic disulfide  $R-S-S-R'$	+0.2	2472.9	Waldo <i>et al.</i> (1991) <sup>28</sup>
		2472.8	Morra <i>et al.</i> (1997) <sup>15</sup>
		2473.0	Vairavamurthy <i>et al.</i> (1997) <sup>23</sup>
		2472.1	Rompel <i>et al.</i> (1998) <sup>31</sup>
		2472.7	Xia <i>et al.</i> (1998) <sup>32</sup>
		2473.2	Schroth <i>et al.</i> (2007) <sup>33</sup>
		2472.5	Lemelle <i>et al.</i> (2008) <sup>26</sup>
		2473.2	Cai <i>et al.</i> (2009) <sup>29</sup>
		2472.6	Prietzl <i>et al.</i> (2009) <sup>18</sup>
		2472.6	Almkvist <i>et al.</i> (2010) <sup>30</sup>
		2472.7	Orthous-Daunay <i>et al.</i> (2010) <sup>19</sup>
		2472.7	Prietzl <i>et al.</i> (2011) <sup>20</sup>
		2473.0	Hoffmann <i>et al.</i> (2012) <sup>21</sup>
		2473.1	Manceau and Nagy (2012) <sup>27</sup>
<b>2472.8 (<math>\pm 0.3</math>)</b>		<b>Mean (<math>\pm SD</math>)</b>	

**Table S1. Sulfur functionality, oxidation state, and white-line peak (continued)**

S functionality	S oxidation state	White-line peak (eV)	References
Thiol	+0.5	2473.5	Waldo <i>et al.</i> (1991) <sup>28</sup>
R—S—H		2473.5	Vairavamurthy <i>et al.</i> (1995) <sup>14</sup>
		2473.5	Vairavamurthy <i>et al.</i> (1997) <sup>23</sup>
		2473.5	Xia <i>et al.</i> (1998) <sup>32</sup>
		2473.4	Bostick <i>et al.</i> (2005) <sup>16</sup>
		2473.2	Lemelle <i>et al.</i> (2008) <sup>26</sup>
		2473.4	Burton <i>et al.</i> (2009) <sup>17</sup>
		2472.3	Cai <i>et al.</i> (2009) <sup>29</sup>
		2473.4	Prietzl <i>et al.</i> (2009) <sup>18</sup>
		2473.4	Almkvist <i>et al.</i> (2010) <sup>30</sup>
		2473.5	Orthous-Daunay <i>et al.</i> (2010) <sup>19</sup>
		2473.5	Prietzl <i>et al.</i> (2011) <sup>20</sup>
		2473.7	Hoffmann <i>et al.</i> (2012) <sup>21</sup>
		2473.4	Manceau and Nagy (2012) <sup>27</sup>
		2473.5	This study <sup>a</sup>
		<b>2473.4 (±0.3)</b>	<b>Mean (±SD)</b>
Organic monosulfide	+0.5	2473.4	Waldo <i>et al.</i> (1991) <sup>28</sup>
R—S—R'		2473.4	Vairavamurthy <i>et al.</i> (1995) <sup>14</sup>
		2473.1	Morra <i>et al.</i> (1997) <sup>15</sup>
		2473.5	Vairavamurthy <i>et al.</i> (1997) <sup>23</sup>
		2473.1	Rompel <i>et al.</i> (1998) <sup>31</sup>
		2473.7	Xia <i>et al.</i> (1998) <sup>32</sup>
		2473.5	Sarret <i>et al.</i> (1999) <sup>24</sup>
		2473.8	Schroth <i>et al.</i> (2007) <sup>33</sup>
		2473.3	Lemelle <i>et al.</i> (2008) <sup>26</sup>
		2473.4	Burton <i>et al.</i> (2009) <sup>17</sup>
		2472.7	Cai <i>et al.</i> (2009) <sup>29</sup>
		2473.4	Prietzl <i>et al.</i> (2009) <sup>18</sup>
		2473.6	Almkvist <i>et al.</i> (2010) <sup>30</sup>
		2473.3	Orthous-Daunay <i>et al.</i> (2010) <sup>19</sup>
		2473.6	Hoffmann <i>et al.</i> (2012) <sup>21</sup>
		2473.7	Manceau and Nagy (2012) <sup>27</sup>
		2473.7	This study <sup>a</sup>
		<b>2473.4 (±0.3)</b>	<b>Mean (±SD)</b>

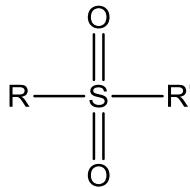
<sup>a</sup> L-cysteine as the reference material. <sup>b</sup> L-methionine as the reference material.

**Table S1. Sulfur functionality, oxidation state, and white-line peak (continued)**

S functionality	S oxidation state	White-line peak (eV)	References
Thiophene 	+1	2474.1	Waldo <i>et al.</i> (1991) <sup>28</sup>
		2473.9	Vairavamurthy <i>et al.</i> (1994) <sup>22</sup>
		2473.8	Vairavamurthy <i>et al.</i> (1995) <sup>14</sup>
		2473.0	Sarret <i>et al.</i> (1999) <sup>24</sup>
		2473.9	Lemelle <i>et al.</i> (2008) <sup>26</sup>
		2473.0	Cai <i>et al.</i> (2009) <sup>29</sup>
		2474.1	Manceau and Nagy (2012) <sup>27</sup>
		2474.5	This study <sup>a</sup>
		2473.8 ( $\pm 0.5$ )	Mean ( $\pm SD$ )
Sulfoxide 	+2	2476.1	Waldo <i>et al.</i> (1991) <sup>28</sup>
		2475.0	Vairavamurthy <i>et al.</i> (1994) <sup>22</sup>
		2475.9	Vairavamurthy <i>et al.</i> (1995) <sup>14</sup>
		2476.0	Vairavamurthy <i>et al.</i> (1997) <sup>23</sup>
		2475.9	Rompel <i>et al.</i> (1998) <sup>31</sup>
		2476.0	Xia <i>et al.</i> (1998) <sup>32</sup>
		2476.0	Sarret <i>et al.</i> (1999) <sup>24</sup>
		2475.6	Schroth <i>et al.</i> (2007) <sup>33</sup>
		2475.4	Cai <i>et al.</i> (2009) <sup>29</sup>
		2475.8	Prietzl <i>et al.</i> (2009) <sup>18</sup>
		2476.0	Almkvist <i>et al.</i> (2010) <sup>30</sup>
		2476.7	Orthous-Daunay <i>et al.</i> (2010) <sup>19</sup>
		2476.2	Prietzl <i>et al.</i> (2011) <sup>20</sup>
		2476.4	Hoffmann <i>et al.</i> (2012) <sup>21</sup>
		2476.4	Manceau and Nagy (2012) <sup>27</sup>
		2476.3	This study <sup>b</sup>
		2476.0 ( $\pm 0.4$ )	Mean ( $\pm SD$ )
Sulfite $\text{SO}_3^{2-}$	+3.68	2478.6	Vairavamurthy <i>et al.</i> (1995) <sup>14</sup>
		2477.6	Cai <i>et al.</i> (2009) <sup>29</sup>
		2478.7	Prietzl <i>et al.</i> (2009) <sup>18</sup>
		2478.3	Almkvist <i>et al.</i> (2010) <sup>30</sup>
		2478.3	Orthous-Daunay <i>et al.</i> (2010) <sup>19</sup>
		2478.5	Prietzl <i>et al.</i> (2011) <sup>20</sup>
		2478.5	Manceau and Nagy (2012) <sup>27</sup>
		2478.4 ( $\pm 0.4$ )	Mean ( $\pm SD$ )

<sup>a</sup> 2-Thiophenecarboxylic acid as the reference material. <sup>b</sup> DL-methionine sulfoxide as the reference material.

**Table S1. Sulfur functionality, oxidation state, and white-line peak (continued)**

S functionality	S oxidation state	White-line peak (eV)	References
Thiosulfate	-1, +5	2472.1, 2480.8 2471.9, 2480.6	Vairavamurthy <i>et al.</i> (1993) <sup>34</sup> Vairavamurthy <i>et al.</i> (1995) <sup>14</sup>
$\text{S}_2\text{O}_3^{2-}$		2472.0, 2481.2 2471.9, 2480.5 2471.5, 2480.8 -----, 2480.1 2472.5, 2479.3	Morra <i>et al.</i> (1997) <sup>15</sup> Bostick <i>et al.</i> (2005) <sup>16</sup> Burton <i>et al.</i> (2009) <sup>17</sup> Cai <i>et al.</i> (2009) <sup>29</sup> Almkvist <i>et al.</i> (2010) <sup>30</sup>
		<b>2472.0 (<math>\pm 0.3</math>), 2480.5 (<math>\pm 0.6</math>)</b>	<b>Mean (<math>\pm \text{SD}</math>)</b>
Sulfone	+4	2480.1 2480.5 2480.5 2480.1 2480.0 2480.5 2479.0 2480.2 2480.6 2480.1 2480.5 2479.6 2480.9	Waldo <i>et al.</i> (1991) <sup>28</sup> Vairavamurthy <i>et al.</i> (1995) <sup>14</sup> Vairavamurthy <i>et al.</i> (1997) <sup>23</sup> Xia <i>et al.</i> (1998) <sup>32</sup> Sarret <i>et al.</i> (1999) <sup>24</sup> Bostick <i>et al.</i> (2005) <sup>16</sup> Cai <i>et al.</i> (2009) <sup>29</sup> Prietzl <i>et al.</i> (2009) <sup>18</sup> Almkvist <i>et al.</i> (2010) <sup>30</sup> Orthous-Daunay <i>et al.</i> (2010) <sup>19</sup> Prietzl <i>et al.</i> (2011) <sup>20</sup> Manceau and Nagy (2012) <sup>27</sup> This study <sup>a</sup>
		<b>2480.2 (<math>\pm 0.5</math>)</b>	<b>Mean (<math>\pm \text{SD}</math>)</b>

<sup>a</sup> Sulfanilamide as the reference material.

**Table S1. Sulfur functionality, oxidation state, and white-line peak (continued)**

S functionality	S oxidation state	White-line peak (eV)	References
Sulfonate 	+5	2481.2 2481.2 2481.1 2481.5 2481.2 2481.0 2481.2 2481.5 2480.4 2481.3 2481.1 2481.1 2481.3 2481.2 2481.3 2481.2	Waldo <i>et al.</i> (1991) <sup>28</sup> Vairavamurthy <i>et al.</i> (1994) <sup>22</sup> Vairavamurthy <i>et al.</i> (1995) <sup>14</sup> Vairavamurthy <i>et al.</i> (1997) <sup>23</sup> Xia <i>et al.</i> (1998) <sup>32</sup> Sarret <i>et al.</i> (1999) <sup>24</sup> Bostick <i>et al.</i> (2005) <sup>16</sup> Schroth <i>et al.</i> (2007) <sup>33</sup> Cai <i>et al.</i> (2009) <sup>29</sup> Prietzl <i>et al.</i> (2009) <sup>18</sup> Almkvist <i>et al.</i> (2010) <sup>30</sup> Orthous-Daunay <i>et al.</i> (2010) <sup>19</sup> Prietzl <i>et al.</i> (2011) <sup>20</sup> Hoffmann <i>et al.</i> (2012) <sup>21</sup> Manceau and Nagy (2012) <sup>27</sup> This study <sup>a</sup>
		<b>2481.2 (±0.2)</b>	<b>Mean (±SD)</b>
Ester sulfate 	+6	2482.5 2482.5 2482.0 2482.5 2481.4 2482.5 2482.7 2482.6 2482.6	Morra <i>et al.</i> (1997) <sup>15</sup> Vairavamurthy <i>et al.</i> (1997) <sup>23</sup> Sarret <i>et al.</i> (1999) <sup>24</sup> Schroth <i>et al.</i> (2007) <sup>33</sup> Cai <i>et al.</i> (2009) <sup>29</sup> Prietzl <i>et al.</i> (2009) <sup>18</sup> Almkvist <i>et al.</i> (2010) <sup>30</sup> Orthous-Daunay <i>et al.</i> (2010) <sup>19</sup> This study <sup>b</sup>
		<b>2482.4 (±0.4)</b>	<b>Mean (±SD)</b>

<sup>a</sup> 1-Amino-2-naphthol-4-sulfonic acid (ANSA) and DL-homocysteic acid as the reference materials. <sup>b</sup> Sodium dodecyl sulfate (SDS) as the reference material.

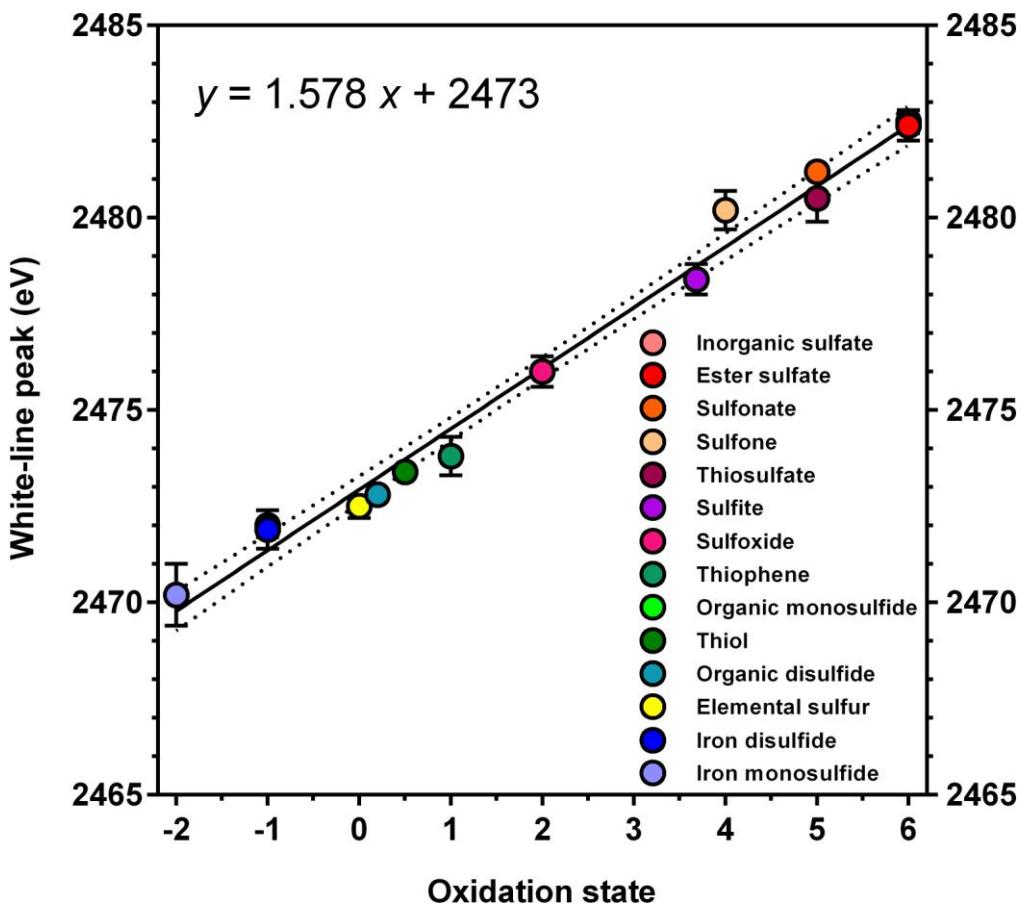
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**Table S1. Sulfur functionality, oxidation state, and white-line peak (continued)**

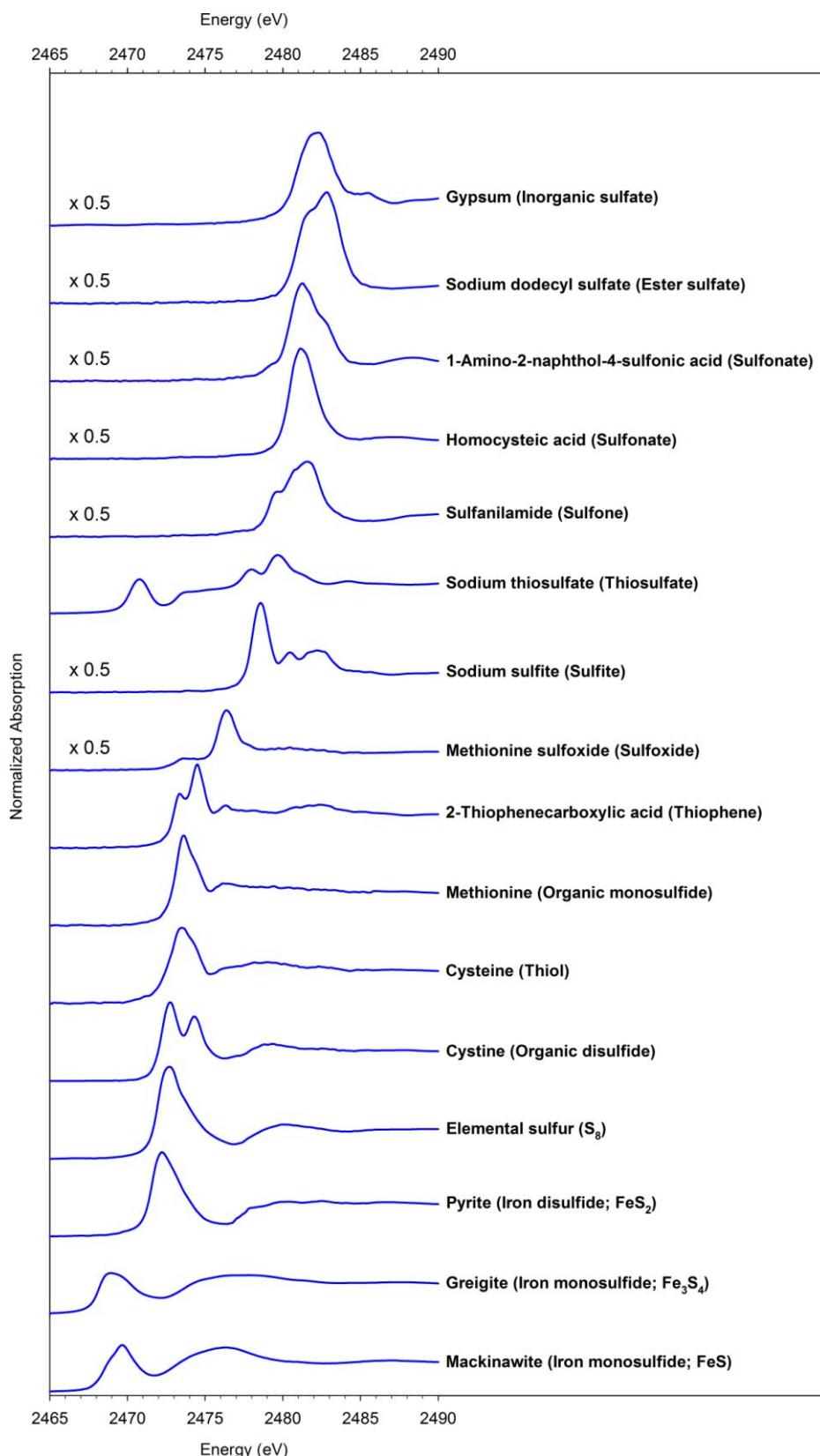
S functionality	S oxidation state	White-line peak (eV)	References
Inorganic sulfate	+6	2482.6	Waldo <i>et al.</i> (1991) <sup>28</sup>
		2482.4	Vairavamurthy <i>et al.</i> (1994) <sup>22</sup>
$\text{SO}_4^{2-}$		2482.0	Vairavamurthy <i>et al.</i> (1995) <sup>14</sup>
		2482.5	Vairavamurthy <i>et al.</i> (1997) <sup>23</sup>
		2482.5	Morra <i>et al.</i> (1997) <sup>15</sup>
		2482.5	Rompel <i>et al.</i> (1998) <sup>31</sup>
		2482.6	Xia <i>et al.</i> (1998) <sup>32</sup>
		2483.0	Sarret <i>et al.</i> (1999) <sup>24</sup>
		2482.3	Bostick <i>et al.</i> (2005) <sup>16</sup>
		2482.5	Lemelle <i>et al.</i> (2008) <sup>26</sup>
		2482.4	Burton <i>et al.</i> (2009) <sup>17</sup>
		2481.8	Cai <i>et al.</i> (2009) <sup>29</sup>
		2482.5	Prietzl <i>et al.</i> (2009) <sup>18</sup>
		2482.4	Almkvist <i>et al.</i> (2010) <sup>30</sup>
		2482.2	Orthous-Daunay <i>et al.</i> (2010) <sup>19</sup>
		2482.7	Prietzl <i>et al.</i> (2011) <sup>20</sup>
		2482.8	Hoffmann <i>et al.</i> (2012) <sup>21</sup>
		2482.7	Manceau and Nagy (2012) <sup>27</sup>
		2482.7	This study <sup>a</sup>
		<b>2482.5 (<math>\pm 0.3</math>)</b>	<b>Mean (<math>\pm SD</math>)</b>

<sup>a</sup> Gypsum as the reference material.

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**Figure S2.** Mean white-line peak energies of S functionalities with different oxidation states. Plotted based on data in Table S1. Error bars represent one standard deviation; where absent, bars fall within symbols. The solid line represents linear regression of all data points ( $R^2 = 0.987$ ) and dotted lines represent the 95% confidence bands.



**Figure S3.** Normalized XANES spectra of S reference compounds. “ $\times 0.5$ ” denotes that the white-line peak intensity of original XANES spectra was scaled down by a factor of two. Raw XANES spectra of greigite, mackinawite, and sodium thiosulfate courtesy of Dr. Edward D. Burton.<sup>17</sup> Raw XANES spectra of L-cystine, elemental sulfur, pyrite, and sodium sulfite courtesy of Dr. Kathryn L. Nagy and Dr. Alain Manceau.<sup>27</sup> Donated XANES spectra (transferability verified) were reprocessed prior to use in this study.

### 3. Chemistry of bulk PPL surface water, sediment porewaters, and sediments (Table S2-S3)

**Table S2. Characteristics of PPL surface water and sediment porewaters**

Bulk surface water					
Sample	pH	[SO <sub>4</sub> <sup>2-</sup> ] (mM)	Σ[S <sup>2-</sup> ] (mM)	[Fe] <sub>T</sub> (μM)	DOC (mM)
P1Jan	8.14 <sup>a</sup>	30.33 ± 0.76 <sup>a</sup>	< 0.01	N.A.	3.25 ± 0.04 <sup>a</sup>
P1Apr	8.38 <sup>a</sup>	19.04 ± 0.01 <sup>a</sup>	< 0.01	< 0.020 <sup>c</sup>	2.99 ± 0.07 <sup>a</sup>
P1Jun	8.35 <sup>a</sup>	19.26 ± 0.31 <sup>a</sup>	< 0.01	N.A.	2.51 ± 0.01 <sup>a</sup>
P8Apr	7.87 <sup>a</sup>	5.17 ± 0.02 <sup>a</sup>	< 0.01	< 0.020 <sup>c</sup>	1.84 ± 0.02 <sup>a</sup>
P8Sep	8.05 <sup>a</sup>	6.95 ± 0.07 <sup>a</sup>	< 0.01	< 0.020 <sup>c</sup>	2.39 ± 0.01 <sup>a</sup>
Bulk sediment porewaters					
Sample	pH	[SO <sub>4</sub> <sup>2-</sup> ] (mM)	Σ[S <sup>2-</sup> ] (mM)	[Fe] <sub>T</sub> (μM)	DOC (mM)
P1Jan	8.58	N.A.	0.58 ± 0.16	N.A.	24.38 ± 0.04
P1Apr	8.62 <sup>a</sup>	1.02 ± 0.01 <sup>b</sup>	2.37 ± 0.03 <sup>a</sup>	0.618 ± 0.046 <sup>b</sup>	6.01 ± 0.03 <sup>a</sup>
P1Jun	7.84 <sup>a</sup>	N.A.	0.89 ± 0.08 <sup>a</sup>	N.A.	8.81 ± 0.02 <sup>a</sup>
P1Sep	7.36 <sup>a</sup>	N.A.	1.95 ± 0.05 <sup>a</sup>	N.A.	9.06 ± 0.02 <sup>a</sup>
P8Apr	8.53 <sup>a</sup>	0.37 ± 0.03 <sup>b</sup>	2.06 ± 0.05 <sup>a</sup>	0.162 ± 0.001 <sup>b</sup>	10.37 ± 0.03 <sup>a</sup>
P8Sep	7.45 <sup>a</sup>	N.A.	1.60 ± 0.06 <sup>a</sup>	N.A.	10.09 ± 0.04 <sup>a</sup>

<sup>a</sup> Data taken from Zeng *et al.* (2011).<sup>11</sup> <sup>b</sup> Data taken from Zeng *et al.* (2012).<sup>35</sup> <sup>c</sup> Data taken from Zeng and Arnold (2013).<sup>36</sup>

**Table S3. Characteristics of PPL sediments**

Analyte <sup>a</sup>	P1Jan	P1Apr	P1Jun	P1Sep	P8Apr	P8Sep
Total sulfur (g/kg) <sup>b</sup>	13.3 ± 0.1	13.3 ± 0.2	13.4 ± 0.1	13.1 ± 0.1	12.5 ± 0.2	12.6 ± 0.2
Organic matter (g/kg) <sup>c</sup>	267 ± 8	262 ± 7	268 ± 8	269 ± 6	265 ± 7	262 ± 8
Total organic carbon (g/kg) <sup>d</sup>	162.0 ± 1.0	162.8 ± 1.3	162.2 ± 1.2	161.7 ± 0.9	159.7 ± 1.9	162.5 ± 1.3
Al (mg/kg) <sup>e</sup>	16218 ± 744	13019 ± 697	13370 ± 603	16937 ± 777	20733 ± 751	20399 ± 836
B (mg/kg) <sup>e</sup>	37.404 ± 0.984	34.693 ± 0.973	35.005 ± 0.821	40.293 ± 0.960	43.449 ± 0.943	46.534 ± 0.825
Ca (mg/kg) <sup>e</sup>	66482 ± 525	69582 ± 581	67528 ± 564	69515 ± 590	77867 ± 609	78682 ± 545
Cd (mg/kg) <sup>e</sup>	0.736 ± 0.098	0.498 ± 0.086	0.469 ± 0.082	0.572 ± 0.076	0.451 ± 0.090	0.654 ± 0.074
Cr (mg/kg) <sup>e</sup>	19.337 ± 1.260	15.452 ± 1.107	16.446 ± 1.072	19.827 ± 1.292	23.340 ± 1.621	23.526 ± 1.533
Cu (mg/kg) <sup>e</sup>	22.645 ± 0.428	22.189 ± 0.519	22.111 ± 0.518	20.746 ± 0.492	22.971 ± 0.534	26.512 ± 0.501
Fe (mg/kg) <sup>e</sup>	18194 ± 105	16964 ± 98	17120 ± 108	17899 ± 113	20783 ± 110	21597 ± 114
K (mg/kg) <sup>e</sup>	4193.8 ± 108.5	3681.6 ± 105.2	3744.0 ± 96.8	4293.4 ± 111.0	5286.0 ± 106.7	5167.7 ± 103.7
Mg (mg/kg) <sup>e</sup>	9396.4 ± 71.7	9246.4 ± 75.4	9200.0 ± 80.5	9522.0 ± 87.7	10825 ± 88.3	11284 ± 82.0
Mn(mg/kg) <sup>e</sup>	1400.4 ± 10.1	1422.8 ± 11.2	1404.2 ± 8.1	1421.2 ± 9.6	1614.5 ± 11.8	1649 ± 12.3
Na (mg/kg) <sup>e</sup>	848.54 ± 9.20	797.20 ± 8.64	791.42 ± 9.58	896.25 ± 9.72	972.16 ± 10.54	992.9 ± 9.95
Ni (mg/kg) <sup>e</sup>	19.041 ± 0.735	17.270 ± 0.866	17.655 ± 0.681	20.507 ± 0.791	21.699 ± 0.737	22.349 ± 0.862
P (mg/kg) <sup>e</sup>	1160.0 ± 22.5	1173.4 ± 22.7	1158.7 ± 20.5	1110.7 ± 21.5	1351.5 ± 24.2	1240.3 ± 21.0
Pb (mg/kg) <sup>e</sup>	9.967 ± 2.157	9.654 ± 1.089	10.522 ± 1.277	8.952 ± 1.937	16.273 ± 2.121	11.092 ± 1.800
Zn (mg/kg) <sup>e</sup>	91.961 ± 0.213	91.069 ± 0.192	90.112 ± 0.211	89.741 ± 0.160	111.31 ± 0.337	102.24 ± 0.226

<sup>a</sup> Data reported on a dry weight basis. Errors represent one standard deviation from duplicate measurements. <sup>b</sup> Determined by dry combustion at 1350°F and subsequent measurement of evolved sulfur dioxide by infrared absorption using a LECO S144-DR sulfur determinator <sup>c</sup> Estimated by loss on ignition at 360°C for 2 h. <sup>d</sup> Determined by dry combustion at 2500°F and subsequent measurement of evolved carbon dioxide by infrared absorption using a Skalar Primacs carbon furnace. <sup>e</sup> Determined by microwave-assisted acid digestion and subsequent measurement of elements in acid-digested aqueous samples by a Perkin-Elmer Optima 3000 inductively coupled plasma-atomic emission spectrometer.

#### **4. Transformations of sedimentary sulfur**

Upon sulfate reduction in sediments, the formed hydrogen sulfide can either undergo re-oxidation, add to organic matter to form organic S, or react with reactive iron to precipitate iron sulfides.<sup>37</sup> Re-oxidation of sulfide can occur at the oxic-anoxic interface via both abiotic and biotic pathways, including chemical oxidation by oxygen, nitrate, or iron and manganese oxides and aerobic or anaerobic oxidation by phototrophic or chemotrophic bacteria.<sup>38</sup> These processes typically regenerate sulfate but also produce a spectrum of intermediate oxidation products, such as elemental sulfur, polysulfides, sulfite, and thiosulfate.<sup>39-43</sup> Most of these reduced inorganic S species, particularly polysulfides, can undergo addition reactions with functionalized organic ligands (e.g.,  $\alpha,\beta$ -unsaturated carbonyls) to form low molecular weight organic S compounds and high molecular weight macromolecules.<sup>44-48</sup> For shallow water bodies, the photochemical sulfurization of functionalized organic matter may also occur in anoxic photic zones.<sup>49</sup> Alternatively, hydrogen sulfide and polysulfides can directly react with dissolved iron(II)<sup>50</sup> or reduce iron(III) (oxyhydr)oxides<sup>51,52</sup> to form metastable iron monosulfides such as greigite ( $\text{Fe}_3\text{S}_{4g}$ ) and mackinawite ( $\text{FeS}_m$ ), as well as more thermodynamically stable pyrite ( $\text{FeS}_{2p}$ ) in the presence of oxygen, elemental sulfur, or other oxidized S intermediates.<sup>53</sup> The reactions of reduced S species with organic matter and iron are competing geochemical pathways, with the latter being more kinetically favored.<sup>54,55</sup> Studies on organic S formation within marine sediments have often documented that the enrichment of S in organic matter is inversely correlated with the availability of reactive iron.<sup>56-59</sup> Reactive iron, however, does not necessarily limit organic S formation in lacustrine and estuarine sediments, because iron sulfides and organic S can concomitantly occur at high levels.<sup>60-63</sup> Quantifying the relative rates of biogeochemical processes is beyond the scope of this study, but the S speciation in PPL sediments is likely to be synchronously controlled by the interactions between the carbon, iron and S cycles.<sup>64</sup>

## 5. Application of sulfur XANES in heterogeneous environmental samples (Table S4)

**Table S4. Qualitative and quantitative S speciation in heterogeneous environmental matrices**

S functionality	Marine sediments	Estuarine sediments	Lacustrine sediments	Riverine sediments	Soils	Organic matter extract
Iron monosulfide (mackinawite, greigite)		Morgan <i>et al.</i> (2012) <sup>65</sup>		Burton <i>et al.</i> (2009) <sup>17</sup>	Burton <i>et al.</i> (2011) <sup>66</sup>	
Iron disulfide (pyrite)	Eglinton <i>et al.</i> (1994) <sup>67</sup> Vairavamurthy <i>et al.</i> (1994) <sup>58</sup> Vairavamurthy <i>et al.</i> (1995) <sup>14</sup>	Morgan <i>et al.</i> (2012) <sup>65</sup>	Bostick <i>et al.</i> (2005) <sup>16</sup> Toevs <i>et al.</i> (2006) <sup>69</sup>	Burton <i>et al.</i> (2009) <sup>17</sup>	Jokic <i>et al.</i> (2003) <sup>68</sup> Prietzl <i>et al.</i> (2003) <sup>70</sup> Prietzl <i>et al.</i> (2009a) <sup>18</sup> Prietzl <i>et al.</i> (2009b) <sup>71</sup> Prietzl <i>et al.</i> (2011a) <sup>20</sup> Prietzl <i>et al.</i> (2011b) <sup>72</sup> Burton <i>et al.</i> (2011) <sup>66</sup>	Morra <i>et al.</i> (1997) <sup>15</sup>
Elemental sulfur	Vairavamurthy <i>et al.</i> (1995) <sup>14</sup>	Morgan <i>et al.</i> (2012) <sup>65</sup>		Burton <i>et al.</i> (2009) <sup>17</sup>	Burton <i>et al.</i> (2011) <sup>66</sup>	Morra <i>et al.</i> (1997) <sup>15</sup>
Organic monosulfide (thiol included)	Eglinton <i>et al.</i> (1994) <sup>67</sup>	Morgan <i>et al.</i> (2012) <sup>65</sup>	Bostick <i>et al.</i> (2005) <sup>16</sup> Toevs <i>et al.</i> (2006) <sup>69</sup>		Martínez <i>et al.</i> (2002) <sup>73</sup> Jokic <i>et al.</i> (2003) <sup>68</sup> Prietzl <i>et al.</i> (2003) <sup>70</sup> Martínez <i>et al.</i> (2007) <sup>74</sup> Prietzl <i>et al.</i> (2007) <sup>25</sup> Schroth <i>et al.</i> (2007) <sup>33</sup> Prietzl <i>et al.</i> (2009a) <sup>18</sup> Prietzl <i>et al.</i> (2009b) <sup>71</sup> Prietzl <i>et al.</i> (2011a) <sup>20</sup> Prietzl <i>et al.</i> (2011b) <sup>72</sup>	Vairavamurthy <i>et al.</i> (1997) <sup>23</sup> Morra <i>et al.</i> (1997) <sup>15</sup> Xia <i>et al.</i> (1998) <sup>32</sup> Solomon <i>et al.</i> (2003) <sup>75</sup> Solomon <i>et al.</i> (2005) <sup>76</sup> Zhao <i>et al.</i> (2006) <sup>77</sup> Einsiedl <i>et al.</i> (2007) <sup>78</sup> Einsiedl <i>et al.</i> (2008) <sup>79</sup> Solomon <i>et al.</i> (2009) <sup>80</sup> Solomon <i>et al.</i> (2011) <sup>81</sup>

**Table S4. Qualitative and quantitative S speciation in heterogeneous environmental matrices (continued)**

S functionality	Marine sediments	Estuarine sediments	Lacustrine sediments	Riverine sediments	Soils	Organic matter extract
Organic disulfide	Eglinton <i>et al.</i> (1994) <sup>67</sup> Vairavamurthy <i>et al.</i> (1994) <sup>58</sup>				Prietzl <i>et al.</i> (2003) <sup>70</sup> Martínez <i>et al.</i> (2007) <sup>74</sup> Prietzl <i>et al.</i> (2007) <sup>25</sup> Prietzl <i>et al.</i> (2009a) <sup>18</sup> Prietzl <i>et al.</i> (2009b) <sup>71</sup> Prietzl <i>et al.</i> (2011a) <sup>20</sup> Prietzl <i>et al.</i> (2011b) <sup>72</sup>	Morra <i>et al.</i> (1997) <sup>15</sup> Vairavamurthy <i>et al.</i> (1997) <sup>23</sup> Hutchison <i>et al.</i> (2001) <sup>82</sup> Solomon <i>et al.</i> (2003) <sup>75</sup> Solomon <i>et al.</i> (2005) <sup>76</sup> Zhao <i>et al.</i> (2006) <sup>77</sup> Einsiedl <i>et al.</i> (2007) <sup>78</sup> Einsiedl <i>et al.</i> (2008) <sup>79</sup> Solomon <i>et al.</i> (2009) <sup>80</sup> Solomon <i>et al.</i> (2011) <sup>81</sup>
Organic polysulfides	Vairavamurthy <i>et al.</i> (1994) <sup>58</sup> Vairavamurthy <i>et al.</i> (1995) <sup>14</sup>				Prietzl <i>et al.</i> (2003) <sup>70</sup>	Vairavamurthy <i>et al.</i> (1997) <sup>23</sup> Solomon <i>et al.</i> (2005) <sup>76</sup> Solomon <i>et al.</i> (2009) <sup>80</sup> Solomon <i>et al.</i> (2011) <sup>81</sup>
Thiophene	Eglinton <i>et al.</i> (1994) <sup>67</sup>				Prietzl <i>et al.</i> (2003) <sup>70</sup>	Xia <i>et al.</i> (1998) <sup>32</sup> Solomon <i>et al.</i> (2003) <sup>75</sup> Solomon <i>et al.</i> (2005) <sup>76</sup> Zhao <i>et al.</i> (2006) <sup>77</sup> Einsiedl <i>et al.</i> (2007) <sup>78</sup> Einsiedl <i>et al.</i> (2008) <sup>79</sup> Solomon <i>et al.</i> (2009) <sup>80</sup> Solomon <i>et al.</i> (2011) <sup>81</sup>

**Table S4. Qualitative and quantitative S speciation in heterogeneous environmental matrices (continued)**

S functionality	Marine sediments	Estuarine sediments	Lacustrine sediments	Riverine sediments	Soils	Organic matter extract
Sulfoxide	Eglinton <i>et al.</i> (1994) <sup>67</sup>				Martínez <i>et al.</i> (2002) <sup>73</sup> Jokic <i>et al.</i> (2003) <sup>68</sup> Prietzl <i>et al.</i> (2003) <sup>70</sup> Martínez <i>et al.</i> (2007) <sup>74</sup> Prietzl <i>et al.</i> (2007) <sup>25</sup> Schroth <i>et al.</i> (2007) <sup>33</sup> Prietzl <i>et al.</i> (2009a) <sup>18</sup> Prietzl <i>et al.</i> (2011a) <sup>20</sup> Prietzl <i>et al.</i> (2011b) <sup>72</sup>	Xia <i>et al.</i> (1998) <sup>32</sup> Solomon <i>et al.</i> (2003) <sup>75</sup> Solomon <i>et al.</i> (2005) <sup>76</sup> Einsiedl <i>et al.</i> (2008) <sup>79</sup> Solomon <i>et al.</i> (2009) <sup>80</sup> Zhao <i>et al.</i> (2006) <sup>77</sup> Solomon <i>et al.</i> (2011) <sup>81</sup>
Sulfite					Martínez <i>et al.</i> (2007) <sup>74</sup> Prietzl <i>et al.</i> (2007) <sup>25</sup> Prietzl <i>et al.</i> (2009a) <sup>18</sup> Prietzl <i>et al.</i> (2009b) <sup>71</sup>	Einsiedl <i>et al.</i> (2007) <sup>78</sup>
Sulfone			Toevs <i>et al.</i> (2006) <sup>69</sup>		Prietzl <i>et al.</i> (2003) <sup>70</sup> Martínez <i>et al.</i> (2007) <sup>74</sup> Prietzl <i>et al.</i> (2007) <sup>25</sup> Prietzl <i>et al.</i> (2009a) <sup>18</sup> Prietzl <i>et al.</i> (2009b) <sup>71</sup> Prietzl <i>et al.</i> (2011a) <sup>20</sup> Prietzl <i>et al.</i> (2011b) <sup>72</sup>	Xia <i>et al.</i> (1998) <sup>32</sup> Einsiedl <i>et al.</i> (2007) <sup>78</sup> Einsiedl <i>et al.</i> (2008) <sup>79</sup>

**Table S4. Qualitative and quantitative S speciation in heterogeneous environmental matrices (continued)**

S functionality	Marine sediments	Estuarine sediments	Lacustrine sediments	Riverine sediments	Soils	Organic matter extract
Sulfonate	Eglinton <i>et al.</i> (1994) <sup>67</sup> Vairavamurthy <i>et al.</i> (1994) <sup>58</sup> Vairavamurthy <i>et al.</i> (1995) <sup>14</sup>	Morgan <i>et al.</i> (2012) <sup>65</sup>	Bostick <i>et al.</i> (2005) <sup>16</sup>		Martínez <i>et al.</i> (2002) <sup>73</sup> Jokic <i>et al.</i> (2003) <sup>68</sup> Prietzl <i>et al.</i> (2003) <sup>70</sup> Martínez <i>et al.</i> (2007) <sup>74</sup> Schroth <i>et al.</i> (2007) <sup>33</sup> Prietzl <i>et al.</i> (2009a) <sup>18</sup> Prietzl <i>et al.</i> (2009b) <sup>71</sup> Prietzl <i>et al.</i> (2011a) <sup>20</sup> Prietzl <i>et al.</i> (2011b) <sup>72</sup> Solomon <i>et al.</i> (2005) <sup>76</sup> Zhao <i>et al.</i> (2006) <sup>77</sup> Einsiedl <i>et al.</i> (2007) <sup>78</sup> Einsiedl <i>et al.</i> (2008) <sup>79</sup> Solomon <i>et al.</i> (2009) <sup>80</sup> Solomon <i>et al.</i> (2011) <sup>81</sup>	Vairavamurthy <i>et al.</i> (1997) <sup>23</sup> Morra <i>et al.</i> (1997) <sup>15</sup> Xia <i>et al.</i> (1998) <sup>32</sup> Hutchison <i>et al.</i> (2001) <sup>82</sup> Solomon <i>et al.</i> (2003) <sup>75</sup> Solomon <i>et al.</i> (2005) <sup>76</sup> Zhao <i>et al.</i> (2006) <sup>77</sup> Einsiedl <i>et al.</i> (2007) <sup>78</sup> Einsiedl <i>et al.</i> (2008) <sup>79</sup> Solomon <i>et al.</i> (2009) <sup>80</sup> Solomon <i>et al.</i> (2011) <sup>81</sup>
Sulfate (ester and inorganic)	Eglinton <i>et al.</i> (1994) <sup>67</sup> Vairavamurthy <i>et al.</i> (1994) <sup>58</sup> Vairavamurthy <i>et al.</i> (1995) <sup>14</sup>	Morgan <i>et al.</i> (2012) <sup>65</sup>	Bostick <i>et al.</i> (2005) <sup>16</sup> Toevs <i>et al.</i> (2006) <sup>69</sup>		Martínez <i>et al.</i> (2002) <sup>73</sup> Jokic <i>et al.</i> (2003) <sup>68</sup> Prietzl <i>et al.</i> (2003) <sup>70</sup> Martínez <i>et al.</i> (2007) <sup>74</sup> Prietzl <i>et al.</i> (2007) <sup>25</sup> Schroth <i>et al.</i> (2007) <sup>33</sup> Prietzl <i>et al.</i> (2008) <sup>83</sup> Prietzl <i>et al.</i> (2009a) <sup>18</sup> Prietzl <i>et al.</i> (2009b) <sup>71</sup> Prietzl <i>et al.</i> (2011a) <sup>20</sup> Prietzl <i>et al.</i> (2011b) <sup>72</sup> Burton <i>et al.</i> (2011) <sup>66</sup>	Morra <i>et al.</i> (1997) <sup>15</sup> Vairavamurthy <i>et al.</i> (1997) <sup>23</sup> Xia <i>et al.</i> (1998) <sup>32</sup> Hutchison <i>et al.</i> (2001) <sup>82</sup> Solomon <i>et al.</i> (2003) <sup>75</sup> Solomon <i>et al.</i> (2005) <sup>76</sup> Zhao <i>et al.</i> (2006) <sup>77</sup> Einsiedl <i>et al.</i> (2007) <sup>78</sup> Einsiedl <i>et al.</i> (2008) <sup>79</sup> Solomon <i>et al.</i> (2009) <sup>80</sup> Solomon <i>et al.</i> (2011) <sup>81</sup>

## 6. PCA and LCF of XANES spectra for P1Sep and P8Sep samples (Table S5-S6)

**Table S5. Principal component analysis and target transformation of P1 XANES spectra**

Principal component analysis <sup>a</sup>		Target transformation <sup>c</sup>				
Component	<i>IND</i> <sup>b</sup>	S reference compound	<i>Chi Sq</i>	<i>Rvalue</i>	<i>SPOIL</i>	<i>Quality</i> <sup>d</sup>
Comp1	0.10027	Mackinawite	53.45772	0.05476	15.3222	Unacceptable
Comp2	0.05226	Greigite	55.43212	0.05640	14.8884	Unacceptable
Comp3	0.04777	Pyrite	8.98916	0.00925	2.8183	Good
Comp4 <sup>b</sup>	0.03490	Elemental sulfur	20.99603	0.02195	6.7406	Unacceptable
		L-Cystine	10.40519	0.01095	6.9841	Unacceptable
		L-Cysteine	2.49160	0.00245	2.7052	Good
		L-Methionine	5.22578	0.00515	2.8479	Good
		2-Thiophenecarboxylic acid	11.32625	0.01131	4.7710	Poor
		DL-Methionine sulfoxide	110.26920	0.10001	12.5170	Unacceptable
		Sodium sulfite	258.51737	0.17752	26.7369	Unacceptable
		Sulfanilamide	29.48807	0.01933	2.5604	Good
		Sodium thiosulfate	39.16720	0.04031	9.6037	Unacceptable
		DL-Homocysteic acid	30.48381	0.01646	1.8049	Good
		1-Amino-2-naphthol-4-sulfonic acid (ANSA)	12.00095	0.00671	1.5916	Good
		Sodium dodecyl sulfate (SDS)	26.50926	0.01239	2.7394	Good
		Gypsum	54.57627	0.04257	8.6229	Unacceptable

<sup>a</sup> Performed using all XANES spectra acquired on P1Jan, P1Apr, P1Jun, and P1Sep samples during November 2011 beamtime. <sup>b</sup> Value reached minimum with 4 components <sup>c</sup> Used to test the suitability of each candidate S species for inclusion in LCF given S reference spectrum is one of the components. <sup>d</sup> Value < 1.5 considered excellent, 1.5 - 3 good, 3 - 4.5 fair, 4.5 - 6 poor, and > 6 unacceptable.

**Table S6. LCF of P1Sep and P8Sep XANES spectra<sup>a</sup>**

Point of interest	Comp1	Fraction1	Comp2	Fraction2	Comp3	Fraction3	Comp4	Fraction4	Sum	NSS	Energy Shift
P1Sep_spot0	Pyrite	0.02283	Cysteine	0.89945	ANSA	0.11475			1.04	$4.38 \times 10^{-3}$	0.16
P1Sep_spot1	Pyrite	0.09199	Cysteine	0.45269	ANSA	0.10357	SDS	0.36158	1.01	$7.39 \times 10^{-3}$	0.09
P1Sep_spot2	Pyrite	0.38581	Cysteine	0.39899	ANSA	0.05959			0.84	$8.70 \times 10^{-3}$	-0.24
P1Sep_allspots <sup>b</sup>	Pyrite	0.19470	Cysteine	0.56207	ANSA	0.09859	SDS	0.11795	0.97	$4.21 \times 10^{-3}$	0.12
P8Sep_spot0	Cysteine	0.16553	ANSA	0.44824	SDS	0.28519			0.90	$4.20 \times 10^{-3}$	-0.06
P8Sep_spot1	Pyrite	0.36031	Cysteine	0.50510	ANSA	0.05948	SDS	0.02516	0.95	$2.57 \times 10^{-3}$	0.06
P8Sep_spot2	Pyrite	0.07772	Cysteine	0.83750	ANSA	0.11806			1.03	$3.46 \times 10^{-3}$	0.15
P8Sep_spot3	Pyrite	0.47501	Cysteine	0.39504	ANSA	0.03281	SDS	0.02999	0.93	$2.27 \times 10^{-3}$	-0.03
P8Sep_spot4	Cysteine	0.65397	ANSA	0.06764	SDS	0.24962			0.97	$3.85 \times 10^{-3}$	0.04
P8Sep_spot5	Pyrite	0.15820	Cysteine	0.70703	ANSA	0.16238			1.03	$3.11 \times 10^{-3}$	0.20
P8Sep_allspots <sup>b</sup>	Pyrite	0.18695	Cysteine	0.53411	ANSA	0.15721	SDS	0.08798	0.97	$1.97 \times 10^{-3}$	0.07

<sup>a</sup> Linear combination fitting of XANES spectra acquired on P1Sep and P1Sep samples during November 2011 beamtime. Fractions were determined using linear combinations of reference spectra. The fit quality was inferred from the normalized sum-squared residual (NSS). The quantification error was estimated to be  $\pm 10\%$  based on fitting precision and accuracy. <sup>b</sup> Determined by LCF of averaged XANES spectra acquired at different spots on the same sample.

## 7. PCA and LCF of chemical maps and XANES spectra for P1 samples (Table S7-S10)

**Table S7. Principal component analysis and target transformation of P1 XANES spectra**

Principal component analysis <sup>a</sup>		Target transformation <sup>c</sup>				
Component	<i>IND</i>	S reference compound	<i>Chi Sq</i>	<i>Rvalue</i>	<i>SPOIL</i>	<i>Quality<sup>d</sup></i>
Comp1	0.02525	Mackinawite	50.43828	0.05166	5.8463	Poor
Comp2	0.01739	Greigite	50.50878	0.05139	6.1352	Unacceptable
Comp3	0.01359	Pyrite	7.90102	0.00813	1.9381	Good
Comp4	0.01227	Elemental sulfur	18.10042	0.01892	6.1556	Unacceptable
Comp5	0.01098 <sup>b</sup>	L-Cystine	7.47663	0.00787	3.5943	Fair
		L-Cysteine	3.05058	0.00300	1.4527	Excellent
		L-Methionine	9.88791	0.00975	2.0224	Good
		2-Thiophenecarboxylic acid	15.72900	0.01570	2.5613	Good
		DL-Methionine sulfoxide	118.54400	0.10752	7.0625	Unacceptable
		Sodium sulfite	266.04564	0.18268	18.6963	Unacceptable
		Sulfanilamide	48.80931	0.03200	3.3832	Fair
		Sodium thiosulfate	34.90189	0.03592	5.1160	Poor
		DL-Homocysteic acid	17.38154	0.00938	1.04994	Excellent
		1-Amino-2-naphthol-4-sulfonic acid (ANSA)	10.19919	0.00570	0.9333	Excellent
		Sodium dodecyl sulfate (SDS)	13.94573	0.00652	1.3679	Excellent
		Calcium sulfate (Gypsum)	7.89981	0.00616	1.4938	Excellent

<sup>a</sup> Performed using all XANES spectra acquired on P1Jan, P1Apr, P1Jun, and P1Sep samples during May 2012 beamtime. <sup>b</sup> Value reached minimum with 5 components

<sup>c</sup> Performed using 5 principal components as indicated by the *IND* value. <sup>d</sup> Value < 1.5 considered excellent, 1.5 - 3 good, 3 - 4.5 fair, 4.5 - 6 poor, and > 6 unacceptable.

**Table S8. LCF of P1 and P8 multi-energy S chemical maps<sup>a</sup>**

Sample	Comp1	Fraction1	Comp2	Fraction2	Comp3	Fraction3	Comp4	Fraction4	Comp5	Fraction5	Sum	MSE
P1Jan	Pyrite	0.23107	Cysteine	0.43038	Gypsum	0.13290	SDS	0.20565			1.00	$4.85 \times 10^{-2}$
P1Apr	Pyrite	0.24086	Cystine	0.11966	Cysteine	0.43386	SDS	0.20562			1.00	$3.24 \times 10^{-2}$
P1Jun	Pyrite	0.29902	Cysteine	0.14524	Gypsum	0.20697	SDS	0.34877			1.00	$3.18 \times 10^{-2}$
P1Sep	Pyrite	0.12463	Cystine	0.27721	Cysteine	0.46638	ANSA	0.06315	SDS	0.06862	1.00	$2.71 \times 10^{-3}$
P8Apr	Pyrite	0.14217	Cystine	0.36025	Cysteine	0.33069	SDS	0.16689			1.00	$4.34 \times 10^{-2}$
P8Sep	Pyrite	0.14600	Cystine	0.35602	Cysteine	0.32830	ANSA	0.08714	SDS	0.08255	1.00	$4.32 \times 10^{-3}$

<sup>a</sup> Linear combination fitting of multi-energy S chemical maps acquired on P1 and P8 samples during May 2012 beamtime. Fractions were determined using linear combinations of reference spectra. The fit quality was evaluated with the whole-map mean squared error (*MSE*). The quantification error was estimated to be  $\pm 10\%$  based on the degree to which normalized absorption differed for S reference spectra at the chemical map energies used.

**Table S9. LCF of P1 and P8 XANES spectra<sup>a</sup>**

Point of interest	Comp1	Fraction1	Comp2	Fraction2	Comp3	Fraction3	Comp4	Fraction4	Comp5	Fraction5	Sum	NSS	Energy Shift
P1Jan_spot0	Cysteine	0.27169	Gypsum	0.35143	SDS	0.35244					0.98	$9.58 \times 10^{-3}$	-0.25
P1Jan_spot1	Pyrite	0.30995	Cysteine	0.18443	SDS	0.16537					0.66 <sup>c</sup>	$1.51 \times 10^{-2}$	0.12
P1Jan_spot2	Pyrite	0.22577	Cysteine	0.12079	SDS	0.20155					0.55 <sup>c</sup>	$1.51 \times 10^{-2}$	0.14
P1Jan_spot3	Pyrite	0.29440	Cysteine	0.16072	SDS	0.15655					0.61 <sup>c</sup>	$1.46 \times 10^{-2}$	0.13
P1Jan_allspots <sup>b</sup>	Pyrite	0.18870	Cysteine	0.20705	Gypsum	0.04841	SDS	0.21009			0.65 <sup>c</sup>	$4.91 \times 10^{-2}$	-0.04
P1Apr_spot0	Cystine	0.20199	Cysteine	0.59832	SDS	0.19311					0.99	$3.48 \times 10^{-3}$	-0.03
P1Apr_spot1	Cystine	0.14570	Cysteine	0.46311	SDS	0.38258					0.99	$5.10 \times 10^{-3}$	0.08
P1Apr_spot2	Cystine	0.38212	Cysteine	0.60574	SDS	0.11872					1.11	$3.96 \times 10^{-3}$	0.04
P1Apr_spot3	Pyrite	0.31416	Cysteine	0.46724	SDS	0.22636					0.91	$4.14 \times 10^{-3}$	0.02
P1Apr_allspots <sup>b</sup>	Pyrite	0.13358	Cystine	0.13819	Cysteine	0.53249	SDS	0.20270			1.01	$1.84 \times 10^{-3}$	0.08
P1Jun_spot0	Gypsum	0.60344	SDS	0.31360							0.92	$1.30 \times 10^{-2}$	0.27
P1Jun_spot1	Pyrite	0.51884	Cysteine	0.25948	Gypsum	0.11497					0.89	$2.44 \times 10^{-3}$	-0.21
P1Jun_spot2	Pyrite	0.28755	Cysteine	0.55282	SDS	0.23223					1.07	$3.55 \times 10^{-3}$	-0.12
P1Jun_spot3	Pyrite	0.38248	Cysteine	0.20225	Gypsum	0.30137					0.89	$2.13 \times 10^{-2}$	-0.13
P1Jun_allspots <sup>b</sup>	Pyrite	0.35843	Cysteine	0.21261	Gypsum	0.20635	SDS	0.16736			0.94	$6.90 \times 10^{-3}$	0.07
P1Sep_spot0	Cystine	0.15173	Cysteine	0.55147	ANSA	0.17355	SDS	0.02799			1.06	$1.73 \times 10^{-3}$	-0.02
P1Sep_spot1	Pyrite	0.15012	Cystine	0.13319	Cysteine	0.59305	ANSA	0.09267	SDS	0.04115	1.01	$1.63 \times 10^{-3}$	0.03
P1Sep_spot2	Cystine	0.33745	Cysteine	0.56350	ANSA	0.08311	SDS	0.09532			1.08	$2.26 \times 10^{-3}$	-0.09
P1Sep_spot3	Pyrite	0.38513	Cysteine	0.39585	SDS	0.05730					0.84	$7.79 \times 10^{-3}$	-0.34
P1Sep_allspots <sup>b</sup>	Pyrite	0.19450	Cystine	0.15173	Cysteine	0.51533	ANSA	0.10097	SDS	0.04175	1.00	$1.73 \times 10^{-3}$	-0.02

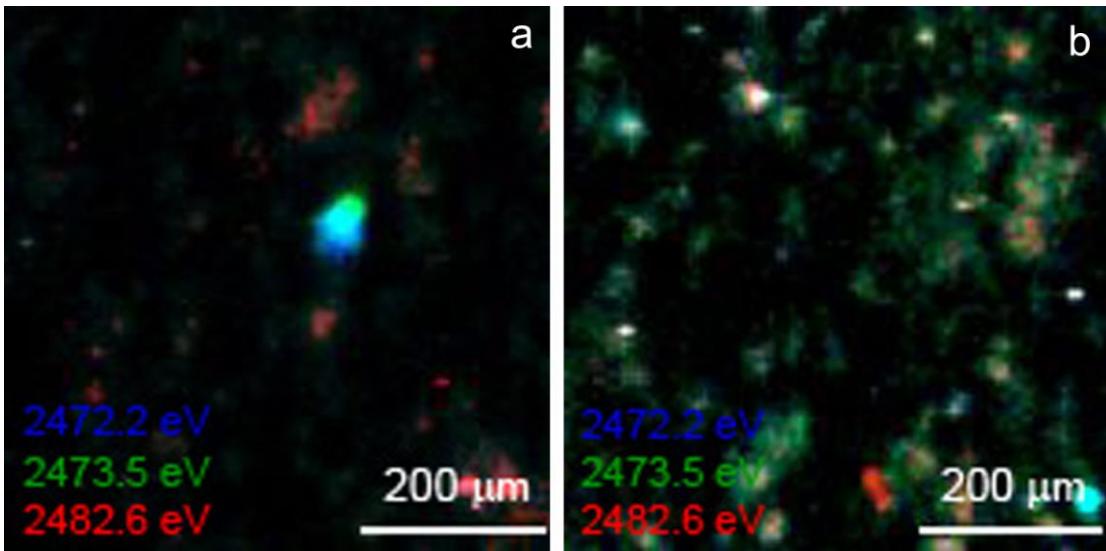
<sup>a</sup> Linear combination fitting of XANES spectra acquired on P1Jan, P1Apr, P1Jun, and P1Sep samples during May 2012 beamtime. Fractions were determined using linear combinations of reference spectra. The fit quality was inferred from the normalized sum-squared residual (NSS). The quantification error was estimated to be  $\pm 10\%$  based on fitting precision and accuracy. <sup>b</sup> Determined by LCF of averaged XANES spectra acquired at different spots on the same sample. <sup>c</sup> Poor sum of the components due to weak signal intensity and poor signal-to-noise ratio.

**Table S10. Fractional contribution of S species in PPL sediments**

Sample	Pyritic S		Reduced organic S		Oxidized S	
	Pyrite (mol%)	Disulfide (mol%)	Monosulfide (mol%) <sup>c</sup>		Sulfonate (mol%)	Sulfate (mol%) <sup>d</sup>
<b>Chemical map fit<sup>a</sup></b>						
P1Jan	23	-	43		-	34
P1Apr	24	12	43		-	21
P1Jun	30	-	15		-	55
P1Sep	12	28	47	6	7	
P8Apr	14	36	33		-	17
P8Sep	15	36	33	9	8	
<b>XANES spectra fit<sup>b</sup></b>						
P1Jan	29	-	32		-	39
P1Apr	13	14	53		-	20
P1Jun	38	-	23		-	39
P1Sep	19	16	51	10	4	

<sup>a</sup> Fractional contribution of S species calculated from LCF of multi-energy S chemical maps in Figure 3 with the sum of all S species normalized to 100 mol%. Error was estimated to be  $\pm 10$  mol%. Raw fitting data presented in Table S8. <sup>b</sup> Fractional contribution of S species from LCF of averaged XANES spectra with the sum of all S species normalized to 100 mol%. Error was estimated to be  $\pm 10$  mol%. Raw fitting data presented in Table S9. <sup>c</sup> Sum of thiol (R-SH) and organic monosulfide (R-S-R'). <sup>d</sup> Sum of ester sulfate (R-O-SO<sub>3</sub><sup>-</sup>) and inorganic sulfate (SO<sub>4</sub><sup>2-</sup>).

**8. Multi-energy S chemical maps of P8Apr and P8Sep samples (Figure S4)**



**Figure S4.** Multi-energy S chemical maps of P8 sediment samples: (a) and (b) tricolor multi-energy S chemical maps (energies at 2472.2 eV, 2473.5 eV, and 2482.6 eV) of P8Apr and P8Sep, respectively.

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